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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

THE SOLUBILITY OF MANGANOUS SULPHATE.

By Theodore William Richards and Frank Roy Fraprie.

Presented by T. W. Richards, March 13, 1901. Received March 21, 1901.

The solubility of manganous sulphate has been carefully determined within the past year by F. G. Cottrell,[*] and the present paper is written to confirm in some measure the results of his work. He was able to disprove by well-considered experiment the less recent work of Linebarger,[†] who published a singular series of results resting upon faulty reasoning and an erroneous method of experimentation. In a case of this kind, when authorities differ, the truth is more quickly enforced when it is supported, hence the publication of the present paper.

The work to be recorded below was done in the spring of 1898, long before the work of Cottrell. It was part of a still unfinished investigation which has as its object the study of the transition equilibria of potassic manganous sulphate. We hope that circumstances may permit the early publication of the remainder of this work, which has been suspended for a time.[‡]

It was soon found that a much higher temperature was necessary to drive off the water of crystallization of manganous sulphate than has usually been supposed. Linebarger used only 180°, at which temperature at least one molecule of water remains in the salt if it is surrounded by air with the usual proportion of aqueous vapor. The handbooks name 210° to 240° as the temperature required, and Cottrell, calling attention to Linebarger's error, used 280°. We found that traces of water still remained after heating for half an hour at 350° in an air bath. In this respect the substance reminds one of cupric sulphate.[§] The amount thus retained does not much exceed the tenth of a per cent, and the effect upon

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[*] Cottrell, J. phys. ch., **4**, 637 (1900).

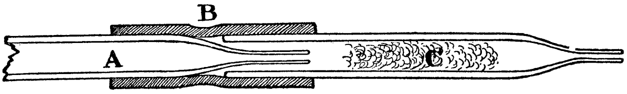
[†] Linebarger. Am. Chem. Journal, **15**, 225 (1893).

[‡] A brief statement of the scope and object of this work will be found in Proc. Am. Ass. Adv. Sc., 213 (1898).

[§] Richards, Proc. Am. Acad., **26**, 240 (1891).

Cottrell's results could not have been serious. On the other hand, a temperature just below redness, perhaps 450°, obtained with a carefully watched naked flame, and applied after long drying at lower temperature, was capable of driving off in five minutes so much of the water that subsequent similar heating for a quarter of an hour showed only an average loss of 0.2 milligram. The product was wholly soluble in water, showing that no decomposition of the sulphate itself had occurred.

The manganous sulphate was purified with great care, and the crystals employed were coarsely powdered. The specimen whose solubility was to be determined was put into a large stout test-tube with a carefully cleaned rubber stopper, and was kept for at least four hours at the desired temperature in an Ostwald thermostat before a sample was taken. The agitation of the mixture was active and continual, being effected by an apparatus similar in principle to that of Schröder.* The motive power was a Henrici hot-air motor. At the close of the appointed time the sample to be analyzed was removed by an effectual filtering pipette, somewhat similar to one which has since been used in van't Hoff's laboratory.† A diagram of the pipette is appended.



FILTERING PIPETTE.

The filtering attachment, filled with cotton wool ("absorbent cotton," C), is temporarily attached to the jet A of a 5-c.c. pipette by means of the rubber tube B.

The cotton was very necessary to filter off the fine powder which appeared during the stirring. In order to avoid change of temperature, the pipette was previously warmed by placing it in a dry test-tube immersed in the thermostat. Only the mouth of the test-tube was allowed to project above the water of the thermostat, and of course every precaution was taken to obtain a fair sample of the solution.

After filling the pipette and quickly removing the rubber filtering-jet attached to it, the clear solution was run into a weighing-bottle and was quickly stoppered and weighed. The known amount of solution was washed into a roomy platinum crucible, when it was cautiously evaporated, and the residue was ignited in the fashion already described. In order to make certain that no transition had occurred during the experiment, the crystal-water contained in the solid phase left over after the saturation was always determined. Below are the data thus obtained.

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* Schröder, Zeitschr. phys. chem., **11**, 454 (1893); Noyes, ibid., **9**, 606 (1892). For details see Richards and Faber, Am. Chem. Journal, **21**, 168 (1899.)

† Van't Hoff and Meyerhoffer, Z. phys. ch., **27**, 79 (1898).

THE SOLUBILITY OF $MnSO_4 . 5H_2O$ AT 25°.

No. of Determination.	Time of Saturation.	Weight of Solution.	Weight of $MnSO_4$.	$MnSO_4$ for 100 gr. Water.
	hours.	grams.	grams.	grams.
1	6	5.0342	1.9849	65.09
2	6	6.3405	2.4947	64.89
3	8	4.4318	1.7470	65.07
4	8	5.2465	2.0656	64.94
			Average	64.99
5	48	3.4514	1.3622	65.20
6	72	3.5349	1.3947	65.17
			Average	65.19

Cottrell found 64.78 as a mean of two closely agreeing determinations, but the time allowed for saturation was only 2.2 hours. The probable reason for his slightly lower result will be discussed below.

The solubility of the tetrahydrate is recorded on the following page.

The solid material taken from the tubes in Determinations 7 to 10 contained as much as 4.3 molecules of water for each $MnSO_4$, but it was nevertheless probably the designated hydrate containing included mother liquor. The greater solubility of the pentahydrate at 30° would certainly involve the solution of any accessible pentahydrate. The salt remaining from determinations 11 and 12 contained 4.03 molecules of water.

The results at 30.15°, giving an average of 66.38, correspond almost exactly with Cottrell's figure 66.43 at 30° ; but in this case his time of saturation was increased to an average of three hours, while ours was not much longer. Hence close correspondence was to have been expected, and the figures mutually support one another. The slight difference may be due to a residual trace of water in Cottrell's salt.

On the other hand, at 35° Cottrell used only two hours for saturation, while we used about seven times as much time. Hence the difference between his result, 67.87, and ours, 68.22, may be explained once more by a difference in the time of mixing.

Until recently the cause of this difference would have been ascribed to a possible incomplete saturation in Cottrell's case ; and the higher figures, other things being equal, would have been accepted as the more accurate.

THE SOLUBILITY OF $MnSO_4.4H_2O$ AT 30.15° AND 35.0°.

No. of Determination.	Temperature.	Time of Saturation.	Weight of Solution.	Weight of $MnSO_4$.	$MnSO_4$ for 100 gr. Water.
		hours.	grams.	grams.	
7	30.15°	4	4.3125	1.7215	66.44
8	30.15°	4	5.7567	2.2943	66.27
9	30.15°	4	4.5992	1.8339	66.32
10	30.15°	4	5.2322	2 0894	66.48
			Average		66.38
11	35.0°	13	3.7009	1.5007	68.21
12	35.0°	14.5	2.7854	1.1296	68.22
			Average		68.22

While this may be true, the recent work of Ostwald* on the solubility of powders and the surface tension of solids has thrown new light on this matter, and it seems quite possible that neither series of results may be perfectly definite. Fine powders have a greater solution-tension than coarse ones, for the same reason that small drops have a greater vapor tension than large ones.

It has often been stated that very long agitation is necessary to secure saturation.† In view of Ostwald's newer work it seems quite possible that continued active agitation introduces an uncertainty even greater than the one which it avoids. The crystals of salt in the ever-moving tube act as mutual millstones, and gradually wear off one another's corners, with the production of fine powder. This fine powder must continually dissolve, because it is more soluble than the larger aggregations. At first it will simply hasten the speed of attaining saturation; but later, when saturation with respect to the larger particles has been attained, the fine powder will tend to produce a solution supersaturated with respect to those larger particles. The experience of Cottrell and others seems to indicate that supersaturation is harder to obviate than inadequate saturation. Cottrell, for example, found that $MnSO_4.H_2O$ attained a concentration of 57.41 grams in 100 grams of water after two hours of agitation when the salt was added to pure water, while after twice as long a time the supersaturation in another tube had only been reduced from 72.5 to 62.3 grams per hundred. The solubility found after 27 hours, when both methods gave the same result, was 58.32, or 0.91 grams more than the first and 4. grams less than the second figure.

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* Ostwald, Z. phys. ch., **34**, 495 (1900).

† For example, see Ostwald's Physicochem. Measurements, Walker (Macmillan, 1894), p. 176.

The outcome of the matter seems to be that constant results upon solubility are usually obtained only when the rate of production of the fine powder exactly balances the rate at which the supersaturation is relieved, and that constant results thus reached represent only a compromise. With cautious agitation, it is possible that a solubility very near that of flat crystal surfaces might be obtained; on the other hand, very active agitation, such as we used, must tend to increase this solubility almost to that corresponding to the fine powder which we always observed in our tubes.

Every one will agree with Ostwald in deciding that the solution tension of flat surfaces, rather than that of sharply curved surfaces, is the quantity which should be determined, if possible. This result would be best obtained by keeping the solid as free as possible from agitation, and driving a constant current of the saturating solution over these resting crystals. A dissolving apparatus which has recently been described, if assisted by a small turbine and suitably immersed in a thermostat, would perhaps be the safest apparatus, although complete saturation would require much time.*

It is evident, as Ostwald points out, that most published determinations of solubility, those of Cottrell and our own included, are subject to a small uncertainty, but it is also evident that the work of Cottrell is by far the most complete work upon the solubility of manganous sulphate which has been published, and that it wholly overthrows the erroneous results of Linebarger.

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* Richards, Am. Chem. Journal, **20**, 189 (1898).

We determined also the solubility of both the dihydrate and the tetrahydrate of the double sulphate of manganese and potassium, and found solutions saturated at 25.0° with both or either hydrate to yield 40.1 grams of anhydrous solid. Hence this temperature must be near the transition temperature of the two hydrates. The detailed publication of these results and many other similar observations must be reserved for a later communication.

In a few words of recapitulation, the present paper may be said to confirm the work of Cottrell and to disprove that of Linebarger, while a measure of doubt is cast upon the usual methods of determining solubility.

CAMBRIDGE, February, 1901.